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# Optimization of positive resist/developer pairs for semiconductor fabrication

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OPTIMIZATION OF POSITIVE RESIST/DEVELOPER  
PAIRS FOR SEMICONDUCTOR FABRICATION

by

John G. Maltabes

A thesis submitted in partial fulfillment  
of the requirements for the degree of  
Bachelor of Science in the School of  
Photographic Arts and Sciences in the  
College of Graphic Arts and Photography  
of the Rochester Institute of Photography

April, 1982

Signature of the Author..... John G. Maltabes 4/24/82.....  
Photographic Science  
and Instrumentation

Certified by..... Mary Ann Hellawell 4/27/82.....  
Thesis Adviser

Accepted by..... Name Illegible 2-1-87.....  
Supervisor, Undergraduate Research

OPTIMIZATION OF POSITIVE RESIST/DEVELOPER  
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Submitted to the  
Photographic Science and Instrumentation Division  
in partial fulfillment of the requirements  
for the Bachelor of Science degree  
at the Rochester Institute of Technology

ABSTRACT

A study was conducted in which a series of experiments were performed using three positive photoresists and three developers in crossed experimentation, simulating semiconductor fabrication steps. Tests conducted, examined coating uniformity, unexposed resist loss, photosensitivity, undercut, and resist flow. Although there was not a clear-cut optimum resist/developer pair, some worked better than others.

ROCHESTER INSTITUTE OF TECHNOLOGY  
COLLEGE OF GRAPHIC ARTS AND PHOTOGRAPHY

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Pairs for Semiconductor Processing

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April 24, 1982

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## INTRODUCTION

Optical lithography is used in the microelectronics industry to delineate patterns to make complex circuits in areas smaller than a square millimeter. Many different techniques are used to form these images. The most widely used today are contact printing, proximity printing, and projection printing methods. A common factor in all the imaging methods is the use of a photoresist which acts as the image receiving material.

The two most widely used resist systems are negative acting resists and positive acting resists. Negative acting resists work by exposed resist polymerizing which renders it insoluble to the developing solvents.<sup>1</sup> Positive acting resists work by increasing the solubility of the exposed resist in an alkaline aqueous solution.<sup>2</sup>

Negative resists currently in use consist of three main components; a binder, a sensitizer, and a carrier. The binder, generally a cyclized polyisoprene polymer is combined with an aryl diazide photoinitiator. When exposed to UV radiation, the aryl diazide reacts with the polyisoprene polymer causing crosslinking to occur, decreasing the solubility of the negative photoresist. The carrier, a blend of organic solvents serves to keep the binder and sensitizer in solution until application.<sup>3</sup> During development of negative photoresist, an organic solvent such as xylene is used to develop away the unexposed resist.

Negative resists are characterized by excellent adhesion, high photospeed, low cost and good resistance to etchants.

Some of the drawbacks of negative resists include image swelling during development, sensitivity to oxygen,<sup>4</sup> and decreased film integrity due to thinner coating requirements. Due to these disadvantages, positive resists are used almost exclusively for image requirements under three microns.<sup>5,6,7</sup>

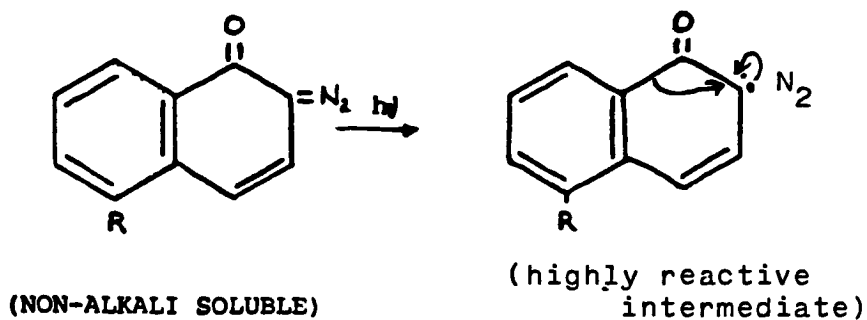
Positive resists generally consist of a base resin,<sup>8</sup> a photoactive compound, and a solvent system.<sup>9</sup> The base resin in a positive resist is commonly a phenol-formaldehyde resin,<sup>10</sup> the photoactive compound, generally a naphthoquinone diazide, acts as an inhibitor to prevent dissolution of the photoresist film. Upon exposure to UV radiation, a photochemical decomposition of the inhibitor occurs (see figure 1), which increases the solubility of the exposed resist in a mild alkaline aqueous developer.<sup>11</sup>

Positive resists are characterized by their ability to provide high resolution, good coverage of steps, good film integrity without pinholes, and the lack of oxygen sensitivity.

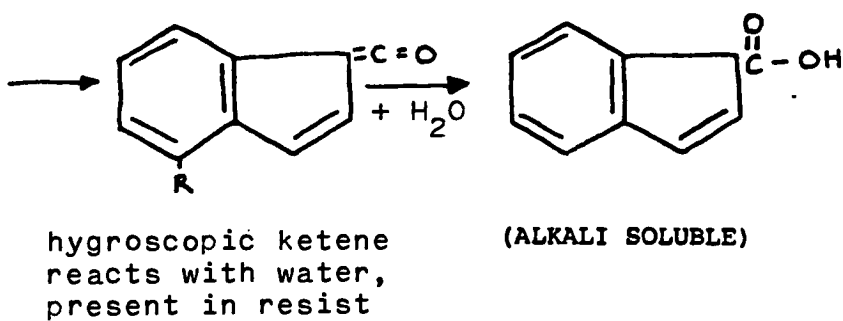
Characterization of positive resists supplied by their manufacturers provide data on the performance of their resists with their developer for that resist. There is no information on how resists of one manufacturer react with the developers of another.

In manufacturing, it is very likely to find several different resists and developers being used to fabricate a given product, depending on what has to be done after a given masking step. The ideal processing condition for this would be to use the same developer for whatever resist is being used, and to have information on the

performance of each resist in a given developer. It is a problem that has not been addressed in depth in the microelectronics industry, but is of interest to many different people and companies.<sup>13,14,15</sup>



R = functional group, frequently a sulfonic acid.



Photochemical decomposition of positive-resist naphthoquinone diazide sensitizer. 16

FIGURE 1

## THE PHOTOLITHOGRAPHIC PROCESS

The purpose of the photolithographic process is to transfer an image from a mask or reticle onto a substrate. The substrate, after resist coating, exposure and development has a pattern defined on it which acts as a stencil for following process steps.

The photolithographic process is made up of ten basic steps.<sup>17</sup>

Table 1

1. Substrate preparation
2. Surface preparation
3. Application of resist
4. Softbake
5. Exposure
6. Development
7. Dry & Rinse
8. Hardbake
9. Etch
10. Resist strip

Substrate preparation is dependant on the process step that is needed for a given device. It is not a photolithographic step. It is the step that preceeds the start of the photolithographic process. It can be a step to deposit a metal, grow a layer of oxide, or deposit some other type of substance.

Surface preparation involves cleaning the wafer surface to remove any contaminants, organic or inorganic, that might

interfere with resist adhesion to the wafer surface. Cleaning involves rinsing the wafer surface with deionized water or a solvent such as trichloroethelene. The wafer is then spun-dry and the surface is blown with nitrogen gas. The wafer then goes through a dehydration baking cycle to remove any moisture from the surface which would interfere with the adhesion of the resist. Bake temperatures range from 250 °C to 600 °C depending on the substrate involved.

Photoresist is applied by dispensing a measured amount through a syringe or similar type of apparatus onto a spinning or stationary wafer. The wafer is then accelerated to the desired spin velocity for the desired time. Final resist film thickness is obtained by varying the spin speed; too low a spin speed will cause a non-uniform coating with the formation of an edge bead, and too high a spin speed will cause a thin coating with poor film integrity.

Prior to coating an organosilane adhesion promoter such as hexamethyldisilazane (HMDS), is used to improve the adhesion of the photoresist to the substrate.<sup>18</sup>

Immediately after the wafers have been coated, they are softbaked to remove any carrier solvents from the coating and to improve resist adhesion. In addition softbaking also helps provide uniform film thicknesses for repeatable exposures as well as harding the film to resist physical damage from handling.

Exposure is accomplished by means of a high intensity ultraviolet radiation source. An image of a mask or reticle is usually projection printed onto the coated substrate,

using either a 1:1 projection alignment system or a step and repeat projection alignment system.

Development can be done by batch processing, where wafers are developed by immersion in the developer, or single wafer processing can be used, where the developer is either sprayed on or allowed to form a puddle on the wafer. Solubility differences between the exposed and unexposed resist areas is on the order of 1000:1, with development being accomplished by use of an alkaline aqueous solution. The rate of development is dependant on time, temperature and agitation. Development is halted by rinsing with deionized water then drying using nitrogen gas.

Hardbaking is done to improve the surface adhesion of the resist and to further increase the resistance to chemical etchants.

The etch step is used to transfer the image defined by the resist onto the underlying substrate. The methods used are wet chemical etching, plasma etching using reactive gas, and reactive ion etching, each with their own advantages and disadvantages.

It is at this point where the photolithographic process and resist have accomplished their purpose, and in order to work on the next layer of whatever device is being made the resist must be stripped from the wafer. This is done using either acids or plasma.

## EXPERIMENTAL PURPOSE

The objectives of this thesis were to design and carry out a series of experiments to determine an optimum positive resist/developer pair for use in semiconductor fabrication. The hypothesis is that the positive resists and developers studied could be used in various combinations to produce different results; greater photospeed, contrast and process latitude. In addition the feasibility of using two resists, a high temperature resist and a normal resist, using the same developer has been studied.



## EXPERIMENTAL PROCEDURE

Three positive photoresists and three developers were obtained from their manufacturers. The resists used were: Shipley 1470, Hunt HPR 204 and Macdermid 9574, and their corresponding developers: Shipley MF-312, Hunt WX-108-5 and Macdermid 9572.

One hundred 4" production quality, bare silicon wafers were obtained to be used as the substrate to coat the resists on. They were initially placed in a plasma etching unit containing an oxygen atmosphere, for thirty minutes, to grow approximately 50 Å of silicon dioxide on the surface to aid in the adhesion of the resist.

Prior to coating, the wafers were cleaned using a Kaspar Uniplane 4000 inline high pressure scrubber unit. The wafers were rinsed with deionized water while they were spinning, scrubbed with deionized water under high pressure, then rinsed again, before being blown dry with nitrogen gas. Immediately after they were cleaned, they went into an infra-red dehydration bake oven, where they were baked at 275 °C for 6 minutes.

Coating was done using a Kaspar Uniplane 4000 inline spin coater. Here the wafers were primed using an adhesion promoter (50% HMDS in cellosolve acetate), puddling the solution onto the wafer surface, allowing it to stand for 10 seconds, then spinning the wafer dry. Immediately following, the resist was dispensed and the wafer accelerated to the proper spin speed to give the desired film thickness. After coating the wafers were softbaked in a Blue M convection

oven, for 30 minutes at 95 °C.

The coated wafers were exposed using a Perkin Elmer Micralign 140 Projection Aligner, and an Optoline inconel alloy on glass, step wedge to attenuate the exposing radiation. The Optoline step wedge has fifteen steps, densities ranging from .21 to 2.00 measured at a wavelength of 550nm  $\pm$  20nm. Within each of the steps are U.S. Air Force resolution targets, with line-space pairs from 10 lp/mm to 500 lp/mm. One unique bar having a size of approximately 6.0 microns was used to be compared to the resist image. The size of this bar was still well within the resolution capability of the projection aligner.

The wafers were batch developed, using a pyrex tank that could hold a gallon of developer. The wafers were held in a teflon wafer carrier that was immersed into the developer. Agitation during development was done by manually rotating the wafer carrier in the developing solution. After development the wafers were placed in a deionized water rinse. The wafers were rinsed for one minute, then placed in a spin dryer under a nitrogen atmosphere.

Hardbaking was done using a Blue M convection oven set at 120 °C and allowing the wafers to bake for thirty minutes.

After the necessary data was collected the resist was stripped from the wafers using a sulfuric acid- hydrogen peroxide bath.

## MEASUREMENT EQUIPMENT

Linewidth measurement of the resist image was made on a Nanometrics Nanoline Critical Dimension Computer at a magnification of 250X, using a 50% threshold for edge detection. Photoresist and SiO<sub>2</sub> film thicknesses were measured using a Nanometrics Nanospec/AFT micro Area Film Thickness Gauge, using a 10X objective. The accuracy of these instruments is within 2% of their displayed values.

## EXPERIMENTAL ANALYSIS

The first experiment performed was designed to look at resist thickness as a function of spin speed, coating uniformity across the wafer and film coating defects. Resist thickness was measured after a 95 °C convection oven softbake, in order to allow the carrier solvents to dry off. The Shipley 1470 resist coatings were uniform and defect at all spin speeds run. The Hunt 204 and Macdermid 9574 resists were not as uniform at the lower coating speeds of 2000 and 3000 rpm. They both displayed the formation of an edge bead at the lower speeds. All three resists did provide low defect striation free coatings.

The experiment designed to determine unexposed resist loss due to development provided unexpected results. The Macdermid 9574 resist was completely stripped from the wafers when immersed in either the Shipley or Hunt developers. There was also no statistically significant resist loss when using the Shipley or Hunt resists in the Macdermid developer. The Shipley developer removed less unexposed resist than the Hunt developer, which appeared to be more active. In all cases, when the resists were coupled with the developers of the same company, the resist loss was less than 8%. The results of this part reduced the resist developer pairs to five.

The next experiment was performed to determine the change in feature size as exposure was changed. Five combinations of resists and developers were run: Shipley resist in Shipley and Hunt developers, Hunt resist in Shipley and Hunt developers, and Macdermid resist with Macdermid developer. One set of wafers, coated with Hunt resist and

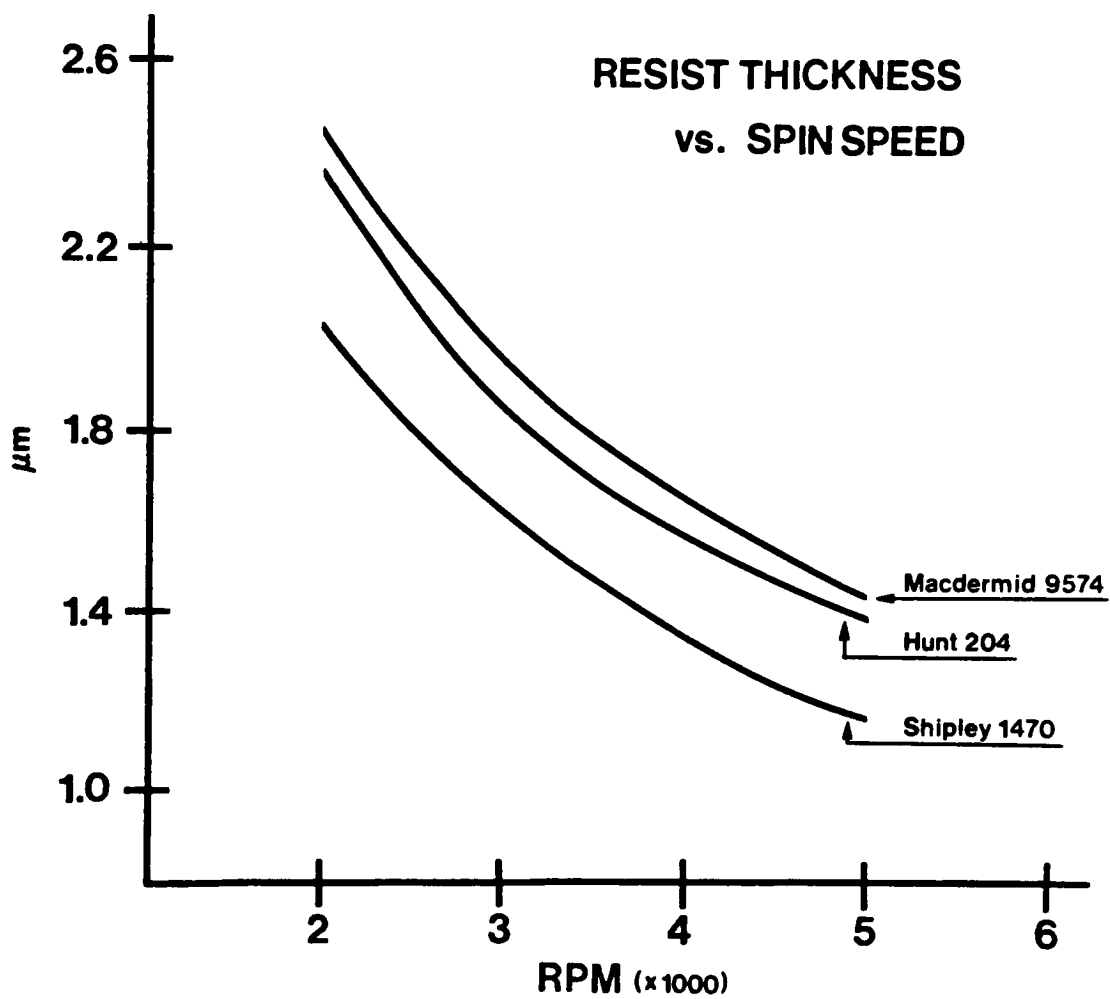


FIGURE 2

developed in the Shipley developer, showed a great deal of scumming in the open image areas which was unacceptable. The Macdermid resist coated wafers required twice the exposure to produce the same feature size as the Hunt or Shipley coated wafers. The Shipley resist coated wafers developed in MF-312 showed the least amount of change in feature size, as exposure was changed. The Hunt resist wafers developed in WX 108-5 showed the greatest degree of change in feature size as exposure was changed. This series determined that the Shipley resist/developer system used could tolerate greater changes in exposure than the Hunt resist/developer pair could, and the Shipley resist with Hunt developer producing an effect between the two.

The effects of undercutting due to a wet chemical etch were then studied. Thirty 4" silicon wafers were placed into a steam diffusion tube to thermally grow a layer of  $\text{SiO}_2$  approximately  $8000\text{\AA}$  thick. The wafers were coated, exposed, processed as before, and linewidths were measured and recorded. The wafers were then baked at  $130^\circ\text{C}$  for 30 minutes prior to being etched in a buffered hydrofluoric acid solution for 6 minutes at  $32^\circ\text{C}$ . After etching, the same linewidths were measured, with the Shipley and Hunt coated wafers showing excellent adhesion to the substrate. The dimensional change for the Hunt and Shipley wafers was .1 microns which was not a statistically significant change in linewidth measurement. The Macdermid coated wafers, on the other hand showed a significant .28 micron change in linewidth.

The last experiment was designed to determine the change in feature size that might occur during a high temperature

DEVIATION FROM DESIRED WINDOW SIZE OPENING  
vs. SCAN SPEED

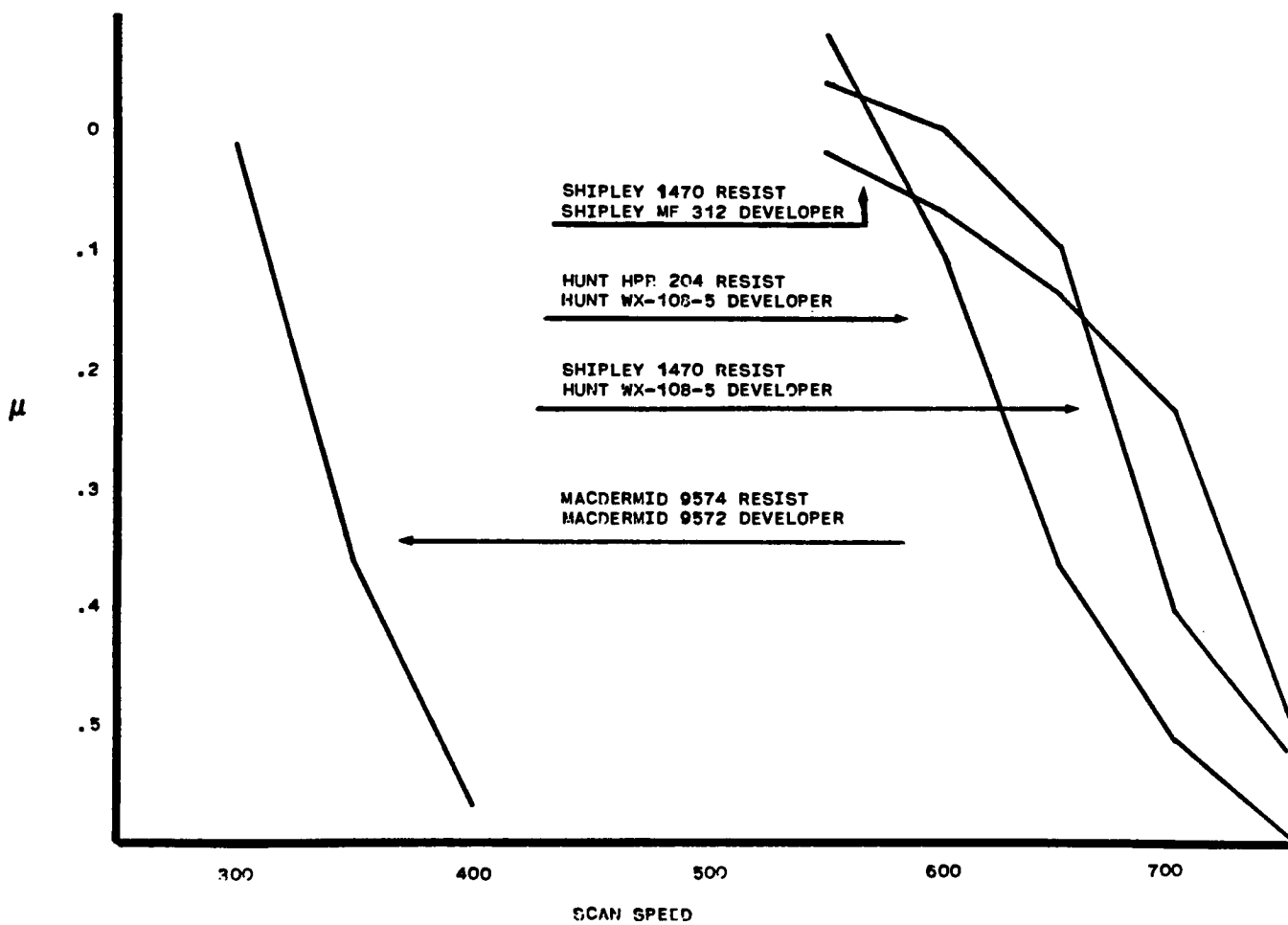


FIGURE 3

process, such as ion implantation or a metal lift-off process. Wafers were coated, exposed, processed and linewidths measured. They were then placed in a convection oven and baked at  $195^{\circ}\text{C}$  for 30 minutes. After baking the linewidths were measured again, with the Hunt and Shipley wafers showing significant changes in feature sizes. The Hunt resist coated wafers showed a change of 10% , and the Shipley resist coated wafers showed a change of 6.5% from the original measurements. The Macdermid resist coated wafers showed no significant dimensional change.



## CONCLUSION

An optimum resist developer pair was not found, however a variety of effects were seen, ranging from minor scumming problems to completely stripping the resist off the wafers during development. All three resists and developers performed well, some better than others.

The Macdermid resist/developer pair performed well in the high temperature process, however it lacked a high photo-speed and was characterized by poor adhesion which caused undercutting during the etch step. In addition the Macdermid resist was not compatible with the Hunt and Shipley developers.

The Hunt and Shipley resists performed similarly, in terms of coating ability, photospeed, adhesion and resist flow. The Hunt developer appeared to be slightly more active, with less tendency to cause scumming than the Shipley developer. Either resist is acceptable for use in semiconductor processing, except when a high temperature step is required.

## REFERENCES

- 1 W.S. DeForest, Photoresist, Materials and Processes, McGraw Hill, 1975
- 2 R.A. Colclaser, Microelectronics: Processing and Device Design, Wiley, 1980
- 3 J.A. McFarland, Jr. and R.F. Leonard, "Modern State-of-the-Art Photoresists-Key to Fine Line Photolithography", Microelectronic Manufacturing and Testing
- 4 S. Mitra, "Recent Developments in Polymeric Resist Materials", Journal of Applied Photographic Engineering
- 5 D.A. Doane "Optical Lithography in the 1 $\mu$ m Limit", Solid State Technology
- 6 J.A. McFarland, Jr. and R.F. Leonard
- 7 P.D. Blais, "A Statistical Model for the Crosslink Density in Negative Type Photoresist Systems", Kodak Microelectronics Seminar Proceedings, Interface'75
- 8 F.H. Dill, et al., "Characterization of Positive Photoresist", IEEE Transactions on Electron Devices
- 9 F.H. Dill, "Optical Lithography", IEEE Transactions on Electron Devices
- 10 J.C. Strieter, "The Chemical Behavior of Positive Working Systems", Kodak Microelectronics Seminar Proceedings, Interface'76
- 11 F.H. Dill, et al.
- 12 D.A. Doane
- 13 R.F. Leonard, Personal communication, July 1981
- 14 G. Miller, Personal communication, July 1981
- 15 J.J. Frankenthaler, Personal communication, July 1981
- 16 J.C. Strieter
- 17 W.S. DeFoerst
- 18 C.A. Deckert and D.A. Peters, "Modes of Photoresist/SiO<sub>2</sub> Adhesion Failure", Kodak Microelectronics Seminar Proceedings, Interface'77

## APPENDIX

Table 2

## RESIST THICKNESS AFTER SOFTBAKE

## Shipley 1470

spin speed(rpm)	2000	3000	4000	5000
mean thickness( $\mu$ )	20.25	16.24	13.36	11.94
standard deviation	.213	.163	.193	.213
sample size	24	24	24	24

## Hunt HPR-204

spin speed(rpm)	2000	3000	4000	5000
mean thickness( $\mu$ )	23.51	18.47	15.76	14.04
standard deviation	.638	.334	.155	.199
sample size	24	24	24	24

## Macdermid 9574

spin speed(rpm)	2000	3000	4000	5000
mean thickness( $\mu$ )	24.39	19.55	16.74	14.41
standard deviation	.663	.246	.161	.123
sample size	24	24	24	24

Table 3

## RESIST LOSS AFTER DEVELOP

Developer	Resist		
	Shipley 1470	Hunt HPR-204	Macdermid 9574
MF-312	.110	.020	---*
WX-108-5	.306	.107	---*
9572	.001 <sup>#</sup>	.006 <sup>#</sup>	.135

\*resist was stripped off wafers by developer

<sup>#</sup> not statistically significant

all measurements in microns

Table 4

## DIMENSIONAL CHANGE DUE TO UNDERCUTTING

resist	before etch( $\mu$ )	after etch( $\mu$ )	change( $\mu$ )
Shipley 1470	5.35	5.45	.10*
Hunt HPR 204	6.11	6.21	.10*
Macdermid 9574	5.97	6.25	.28

8000 Å  $\text{SiO}_2$  etch in buffered HF for 6' @ 32 °C

\*not statistically significant

Table 5

## DIMENSIONAL CHANGE DUE TO HIGH TEMPERATURE PROCESSING

Resist	Window size( $\mu$ )	
	before	after
ShIPLEY 1470	7.72	7.22
Hunt HPR-204	7.29	6.55
Macdermid 9574	5.66	5.64*

\* no statistical significance between before and after data

## VITA

John G. Maltabes, a native of New York City, attended the Bronx High School of Science, prior to attending the Rochester Institute of Technology. While at R.I.T., John studied Photographic Science, and developed an interest in microlithography and semiconductor fabrication. Upon completing his studies at R.I.T., he will join the International Business Machine Corporation in Essex Junction, Vermont.